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Title: Measuring the Properties of Actinide-Molten Salts

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Measuring the Properties of Actinide-Molten Salts

LLNL Chemistry of Nuclear Materials Group
Seminar Series

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Los Alamos National Laboratory

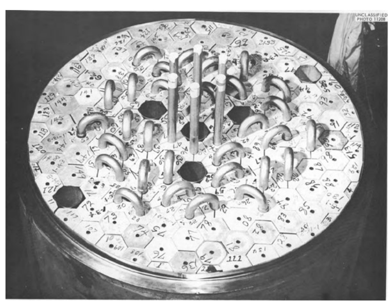
June 4, 2020

Aircraft Reactor Experiment (ARE) and Molten Salt Reactor Experiment (MSRE)

ARE building at ORNL that was retrofitted to house the MSRE.

MSRE graphite core

The NB-36 flew multiple flights in the 1950s carrying an operating MSR; crew worked from a lead-shielded cockpit (12 tons!).



ARE reactor core: BeO moderator blocks and circulating fuel tubes.

- Aircraft Reactor Experiment ("ARE"), 1954, ORNL
  - ARE = 1st reactor to use circulating molten salt fuel
  - For propulsion of supersonic aircraft (!)
- Molten Salt Reactor Experiment (MSRE) @ Oak Ridge National Laboratory (ORNL) was constructed by 1964, went critical in 1965, operated until 1969 *(equivalent to ~1.5 years of full power operation)*
- The MSRE graphite core also moderated it
- **MSRE fuel: LiF-BeF_2-ZrF_4-UF_4** (65-29-5-1; first uranium-235, later uranium-233)
- Its secondary coolant was "FLiBe" (2 LiF-BeF_2)
- Operation temperature: 650 °C

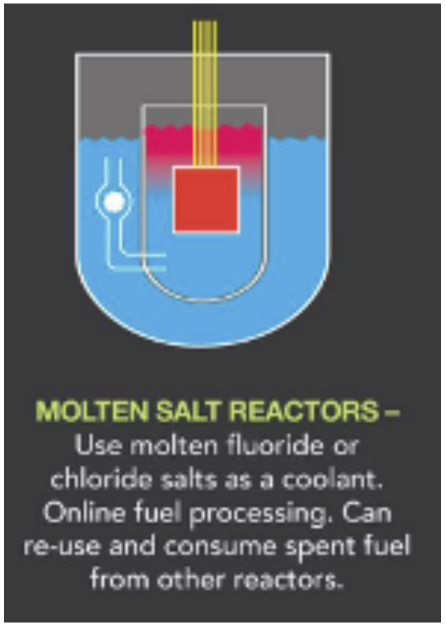
Molten Salt Reactor Fuel: Actinide-Molten Salts

Actinide-molten salt fuel:

Actinide halide(s) dissolved in alkali or alkaline earth metal halide(s) at 450 – 850 ^{o}C

Examples:
- *fluoride system:* ***UF_4 dissolved in LiF-BeF_2-ZrF_4***
- *chloride system:* ***UCl_3 dissolved in NaCl***

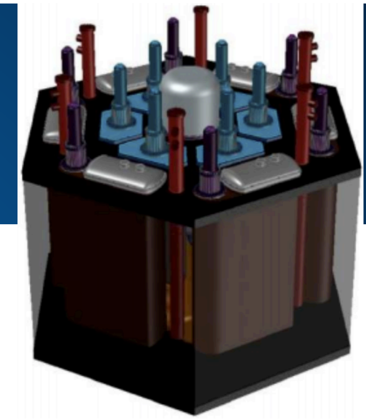
- **Why *liquid* fuel/coolant?**
  - Damage-resistant (release, rather than trap, fission product gases, avoiding damage from high pressures; quick healing)
  - High operating temperature (increased plant efficiency)
- **Why *molten salt*?**
  - Stable at low pressures
  - Low viscosity
  - Good heat transfer properties
  - Good solubility of actinide halide and fission products
  - Conductive
  - Refueling without enrichment
  - Can re-use and consume spent fuel from other reactors
  - Enhanced safety
  - More complete burnup

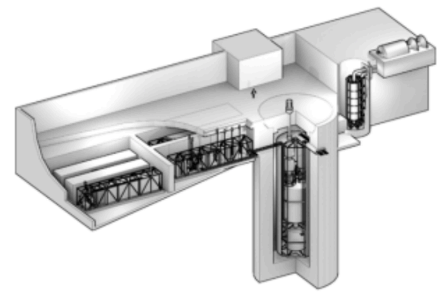


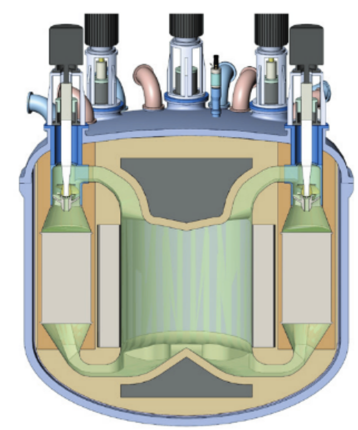
Graphic from US DOE-NE

Growing Number of MSR Developers…and Fuel Salts

Reactor	Fuel Salt
Integral Molten Salt Reactor **Terrestrial Energy, Inc., Canada** thermal	Low enriched **U-, Pu-, Th-, fluoride** or any mixture of these
Compact Molten Salt Reactor **Seaborg Technologies, Denmark** thermal, waste burner	Eutectic **sodium-actinide fluoride**
Copenhagen Atomics Waste Burner **Denmark** thermal, waste burner	**$LiF\text{-}ThF_4$**
ThorCon, Indonesia thermal	**$NaF\text{-}BeF_2\text{-}ThF_4\text{-}UF_4$** (76-12-9.5-2.5)
FUJI International Thorium Molten-Salt Forum, Japan	**$LiF\text{-}BeF_2\text{-}ThF_4\text{-}^{233}UF_4$** (71.76-16-12-0.24) mol%
Stable Salt Reactor **Moltex, United Kingdom** fast spectrum, waste burner	**$NaCl\text{-}PuCl_3\text{-}UCl_3$** (60-20-20) with lanthanide trichlorides
Stable Salt Reactor **Moltex, United Kingdom** thermal	50/50 **UF_3/UF_4 diluted in NaF-RbF**
Liquid Fluoride Thorium Reactor **FLiBe Energy, USA** thermal, breeder	**$LiF\text{-}BeF_2\text{-}UF_4$**
Molten Chloride Fast Reactor **Elysium, TerraPower, both USA** fast spectrum, breeder	**$NaCl\text{-}XCl_z\text{-}UCl_{3/4}\text{-}PuCl_3$**


Elysium's modular MCSFR


FLiBe's "LiFTR"


TerraPower's MCFR

LANL Collaborations and the NE-MSR Landscape

Nuclear Energy (NE) - Molten Salt Reactor (MSR) Landscape

Los Alamos NATIONAL LABORATORY EST. 1943

Actinide (Pu, Th, U) Molten Salt Science

INL Idaho National Laboratory
70 YEARS OF SCIENCE & INNOVATION

Nuclear Engineering, Reactor Demos

MSR Deployment

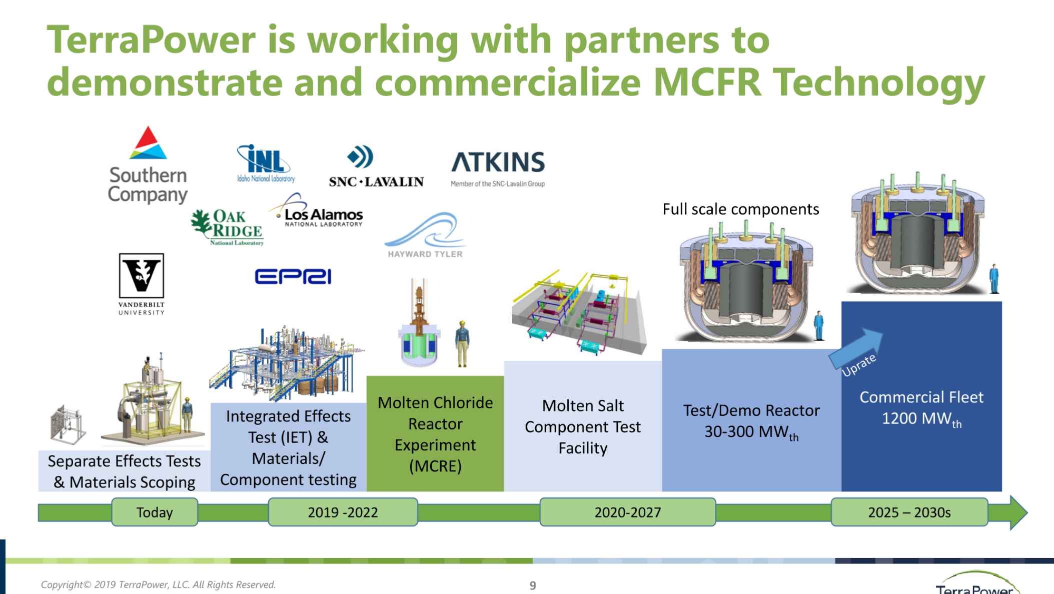
TerraPower
Southern Company
moltex energy
safer, cheaper, cleaner

Reactor Developers and Utilities

OAK RIDGE National Laboratory

Molten Salt Science: Uranium in Molten Fluoride

- **LANL collaborations also include universities, other reactor developers**
- **Other national labs, EFRCs, etc. also in the landscape**



DOE LAUNCHES $230 MILLION ADVANCED REACTOR DEMONSTRATION PROGRAM

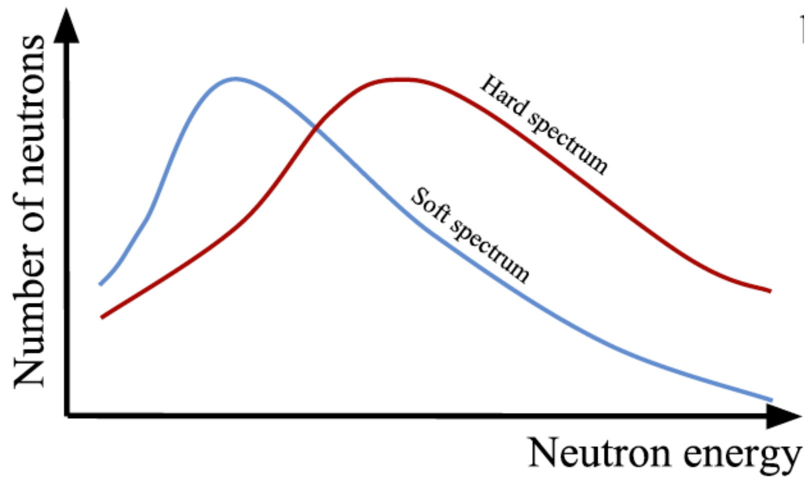
New program designed to help domestic private industry demonstrate advanced nuclear reactors in the United States.

Announced May 14, 2020

Why Chloride Salts?

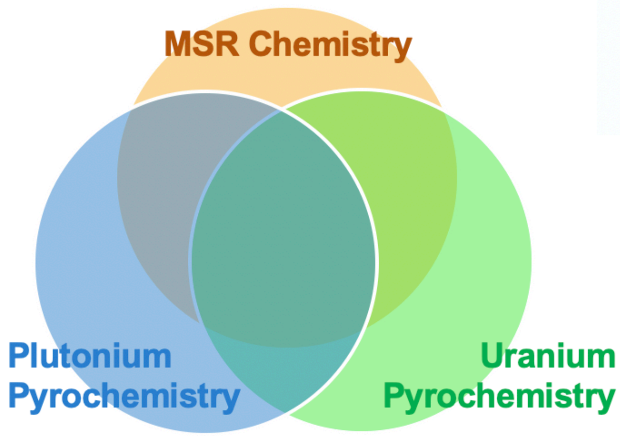
Compared to fluoride salts, chlorides:

- ✓ enable harder neutron spectrum which results in enhanced breeding
- ✓ have better solubility properties: lower melt point solutions with larger amounts of actinide chloride
- ✓ have lower viscosities
- ✓ are more thermally stable
- ✓ are safer
- ✓ are more economically viable to produce



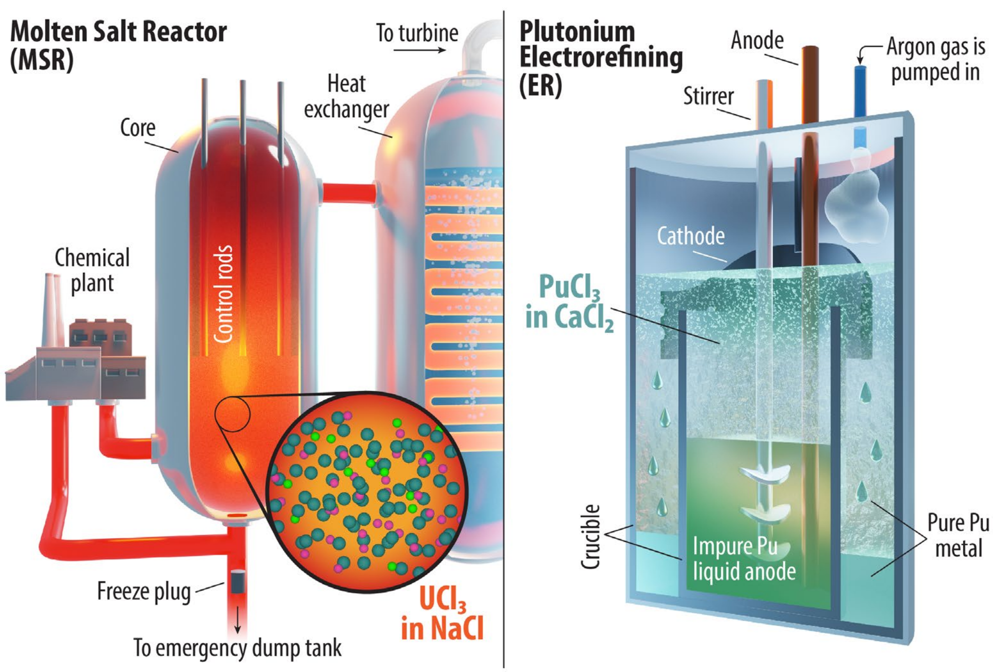
Overlapping areas: MSRs and Actinide Metal Purification

Molten chloride salts have been used for decades in plutonium and high enriched uranium (HEU) purification processes.

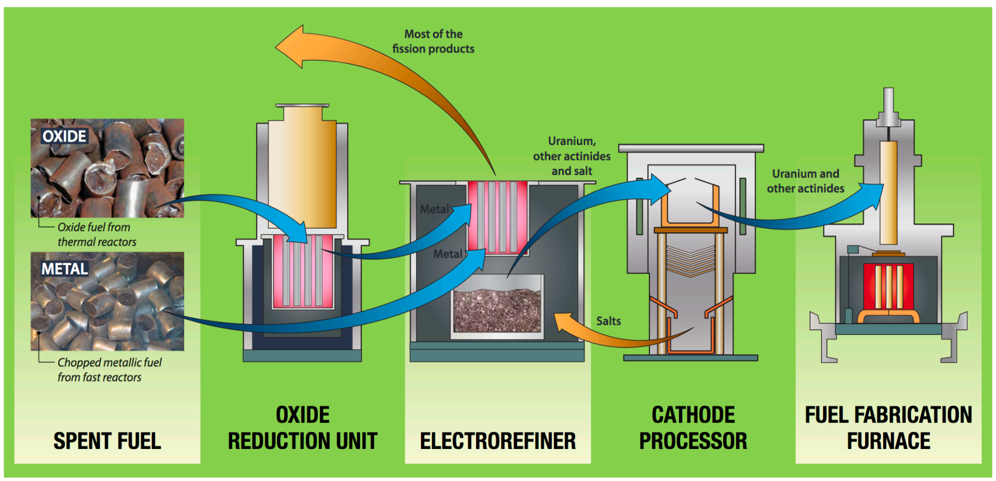


In the intersection:

- Preparation and characterization of solvent salts
- Production of actinide halides (e.g. $PuCl_3$, UCl_3)
- Study of thermophysical properties
- Study of chemical properties
- Evaluating materials of construction in extreme environments
- Development of in-situ diagnostics
- Mitigating side reactions and investigating impurity chemistry
- Identifying signatures and diversionary tactics



An example MSR (left) and plutonium purification @ LANL (right)



Pyroprocessing of spent fuel @ ANL

With Unique Fuel comes Unique Challenges

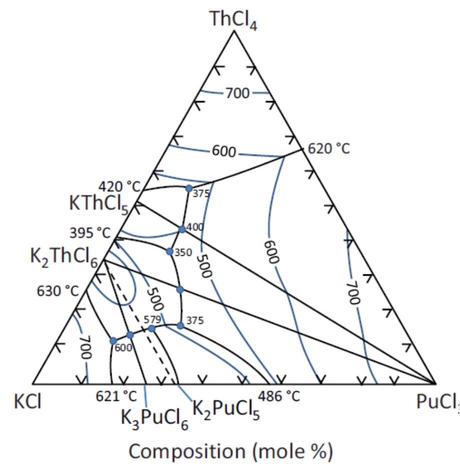
Instead of micro-structure evolution, the challenge for MSRs is chemical evolution due to fission and corrosion products and their impact on chemistry, corrosion, phase equilibria, and thermophysical properties

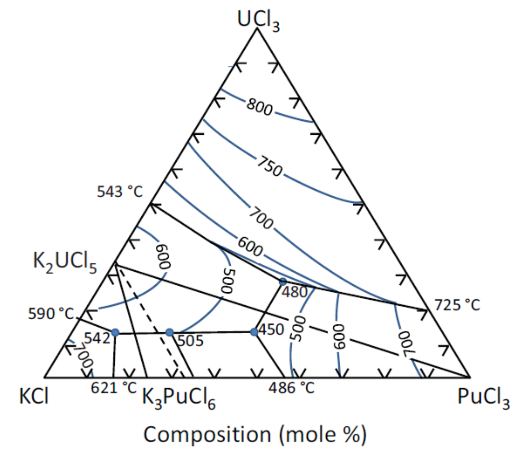
Chemistry: each MSR reactor type, the fuel cycle must be developed and understood with time.

- Noble gasses Xe and Kr can be removed
- Most fission products are soluble. What precipitates? What can be filtered?

Corrosion: Fuel evolution impacts the redox chemistry of the system. This needs to be understood and in some cases mitigated (e.g. MSRE added Be to fuel periodically to keep the solution slightly reducing).

Phase Equilibria:





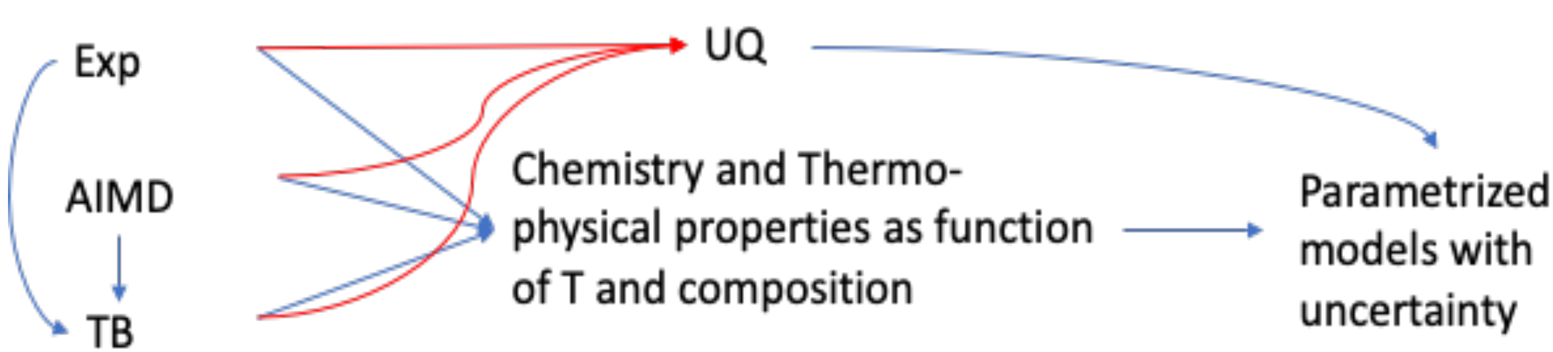
Thermophysical Properties: A robust understanding of composition and temperature dependence needs to be established. Experimental data is lacking (especially for chloride mixtures.

Critical Properties and Our Overall Research Approach

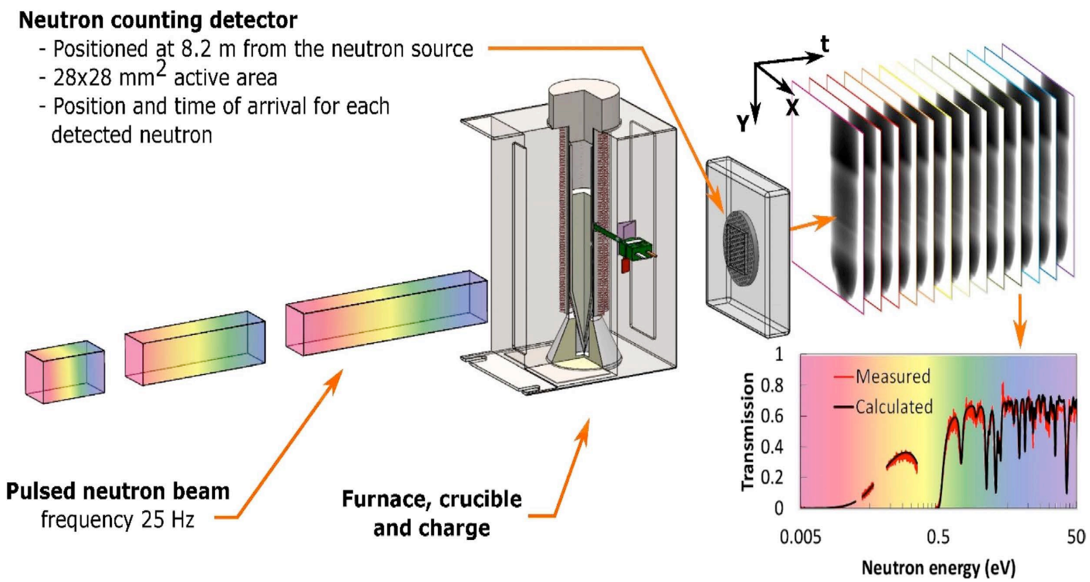
"Verification of the second law of thermodynamics requires four thermophysical property measurements: ***density, thermal conductivity, heat capacity, and viscosity.*** *You need all four or you don't need any"*

- Nicholas Smith, Deputy Directory, National Reactor Innovation Center (INRIC)

Property	Application	Experimental Techniques
Density (ρ)	Thermal Hydraulics, Neutronics	Neutron Radiography; Conventional Dilatometry
Heat Capacity (Cp)	Heat and Energy Transfer	DSC
Viscosity (μ, ν)	Thermal Hydraulics	Dynamic Neutron Radiography; Viscometry
Phase Stability, Solubility	Operating Parameters, Salt Composition	DSC, Drop Calorimetry, ERNI
Thermal Diffusivity (α)	Heat and Energy Transfer	Laser Flash Analysis



Neutron Imaging Capability at LANSCE

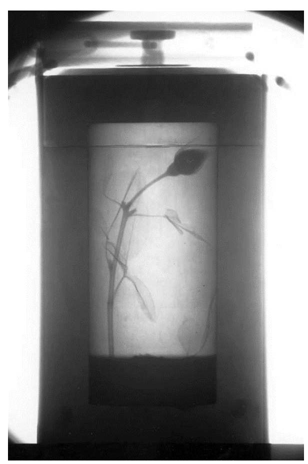


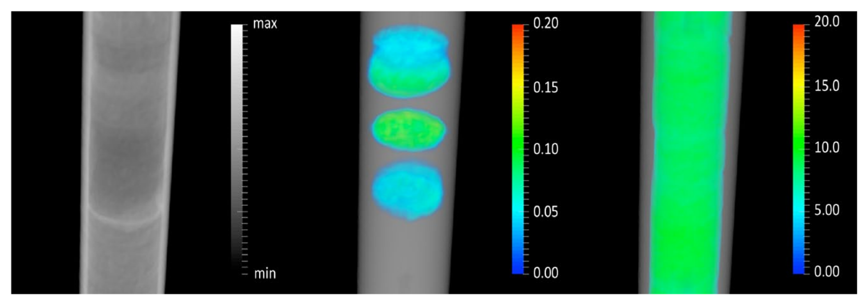
Flat Amorphous Si Panel Specs:

Company/Model:	Varian 2520DX
Active Material:	Amorphous Silicon
Conversion Material:	Gd^2O^2S
Active Area:	19.5 x 24.4 cm
Pixel Matrix:	1,536 x 1,920
Pixel Pitch:	127 μm^2
Frame Rate:	30 fps (half res)

Neutron Beam at FP5:

Neutron Energies:	Thermal - Epithermal
Rep-rate:	20 Hz
D Collimation:	2 cm





Neutron radiography affords the ability to probe large volumes, and observe interaction with both light and heavy elements

Energy Resolved Neutron Imaging (ERNI)

Neutron Radiography with Falling Sphere Technique: Viscosity (η, ν), Density (ρ)

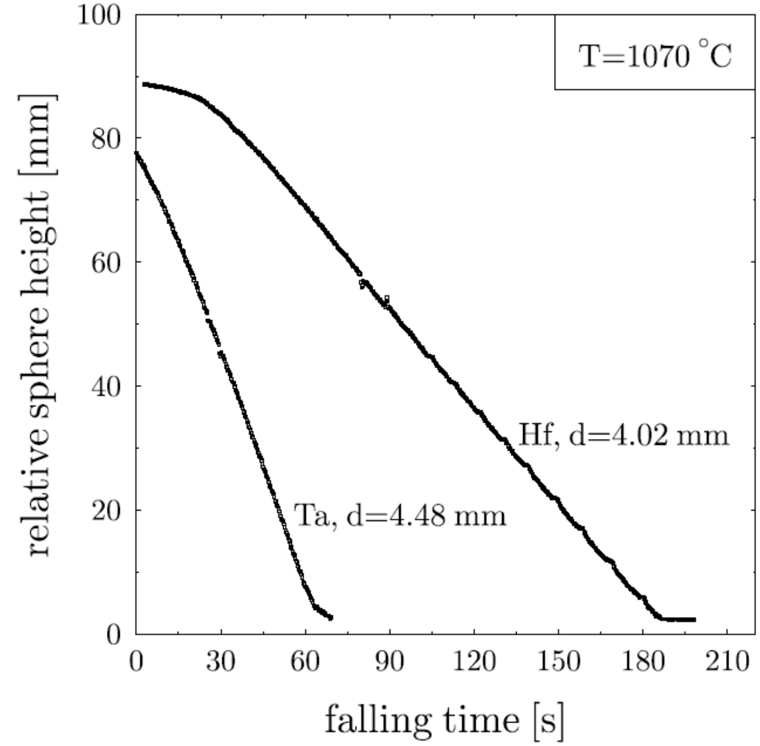
Falling Sphere Viscometry

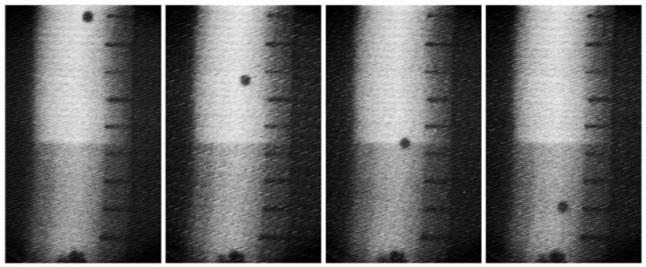
- **Determine viscosity:**
  - Measure the elapsed time required for sphere to fall under gravity through a sample-filled tube
  - Use spheres of two different materials to **derive density** (Stokes' Law)

$$\eta = \frac{2gr^2(\rho_{\text{sphere}} - \rho_{\text{melt}})}{9v}$$

Neutron Radiography

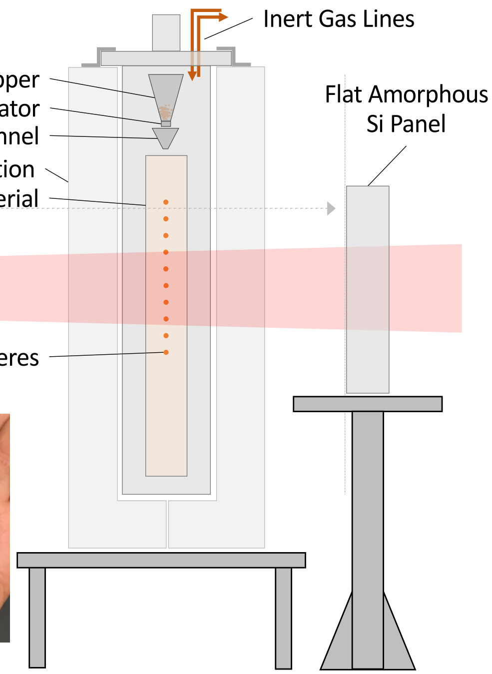
- Dynamic neutron radiography can be used to precisely observe and record spheres falling through molten salt

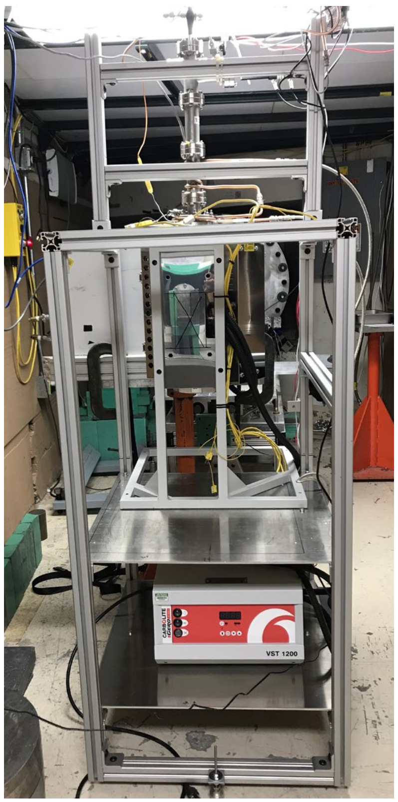


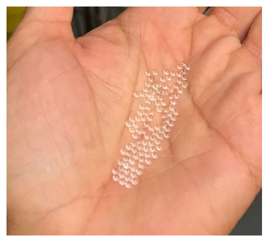


J. Non-Newtonian Fluid Mech. **112** (2003) 203–215

Test Apparatus Installed at LANSCE: ER-2 Flight Path 5







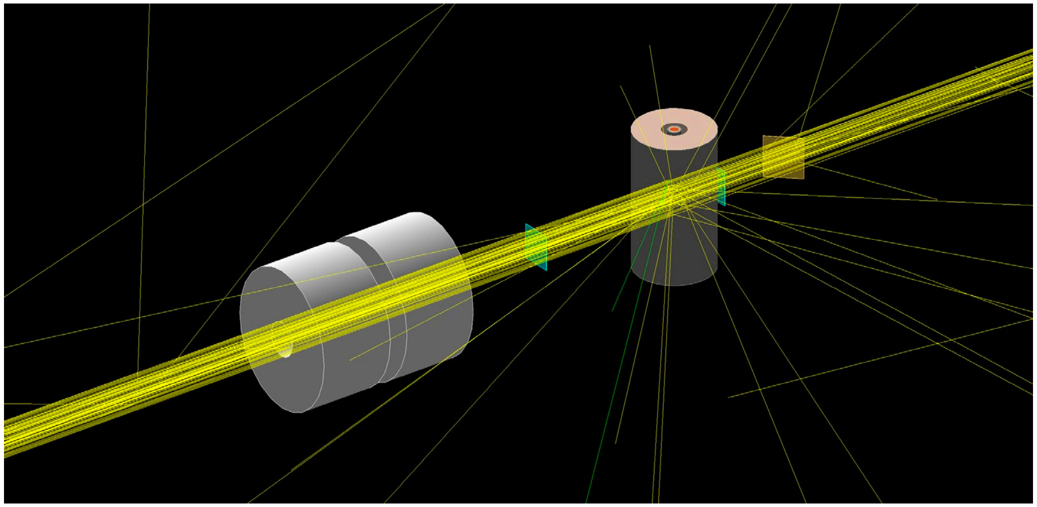
<u>Prototype: Version 1</u>

- Capable of measurements up to 1150 °C
- Active water cooling/cold trap
- Inert gas (argon) environment
- Modular construction

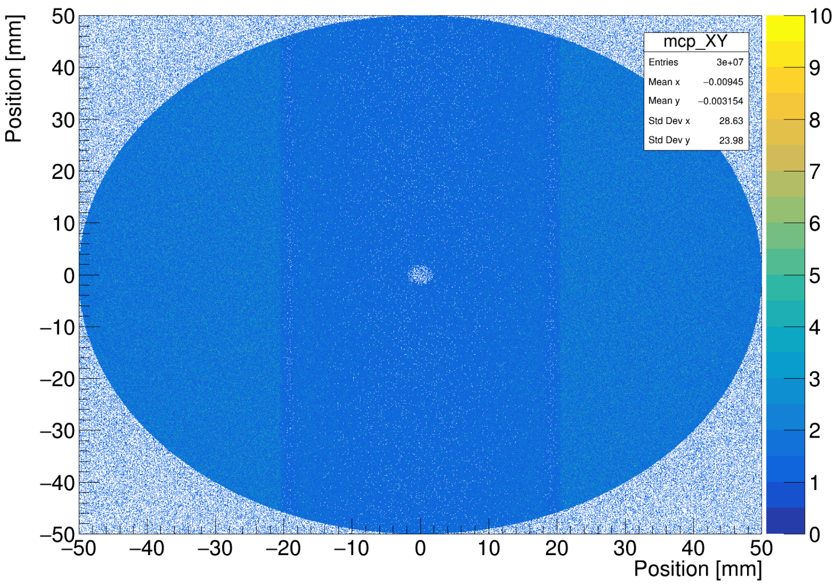
From door of flight path

Beam's perspective

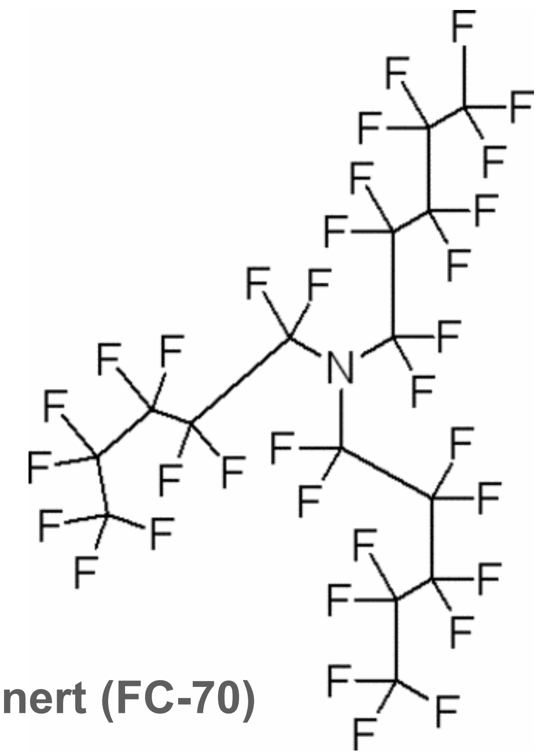
Neutron Beam and Detector Simulations



Simulation of test apparatus in Flight Path 5 at LANSCE, showing neutron beam, collimation, furnace



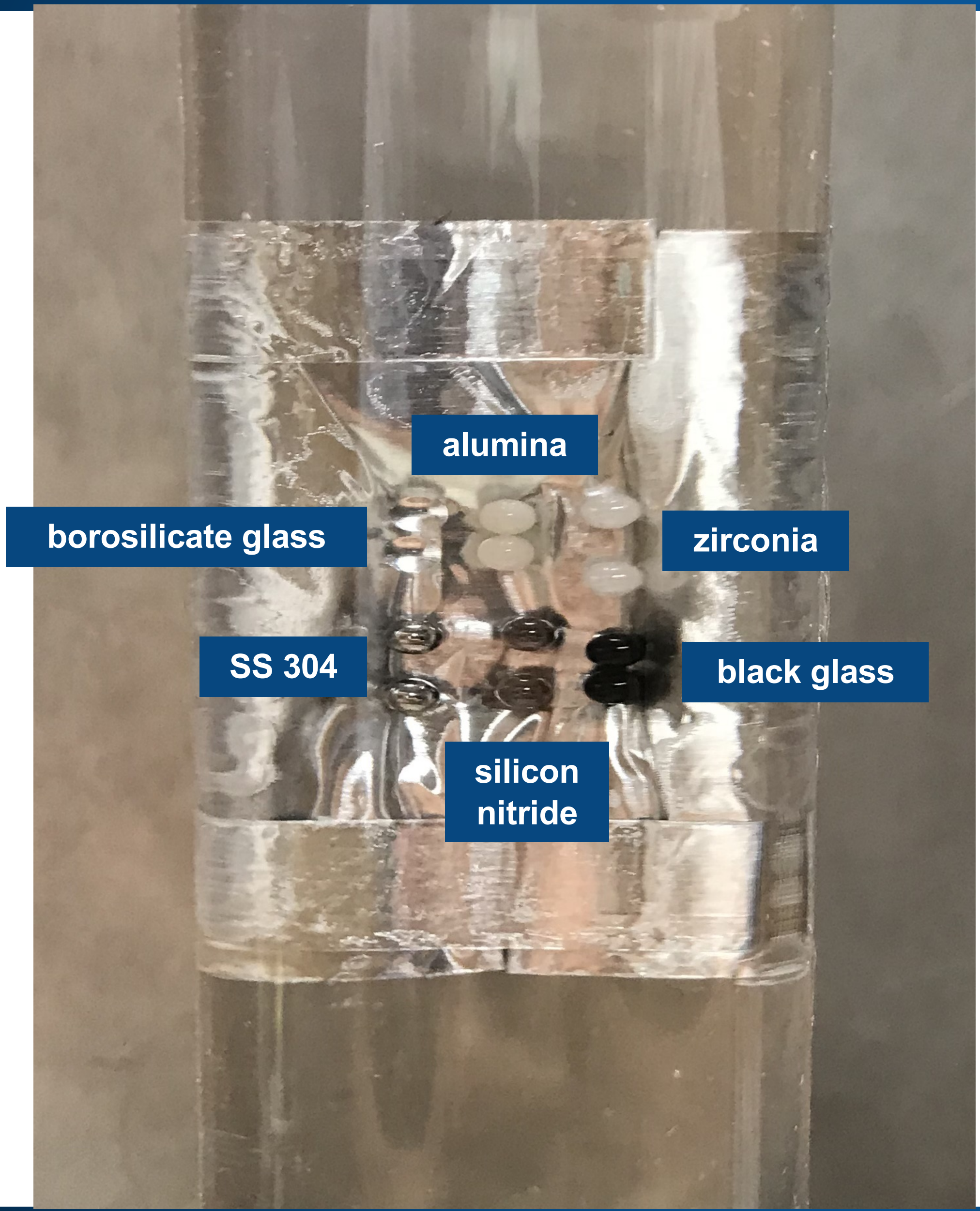
MCNP Simulation: borosilicate sphere within **Fluorinert** standard, quartz tube, in neutron beam

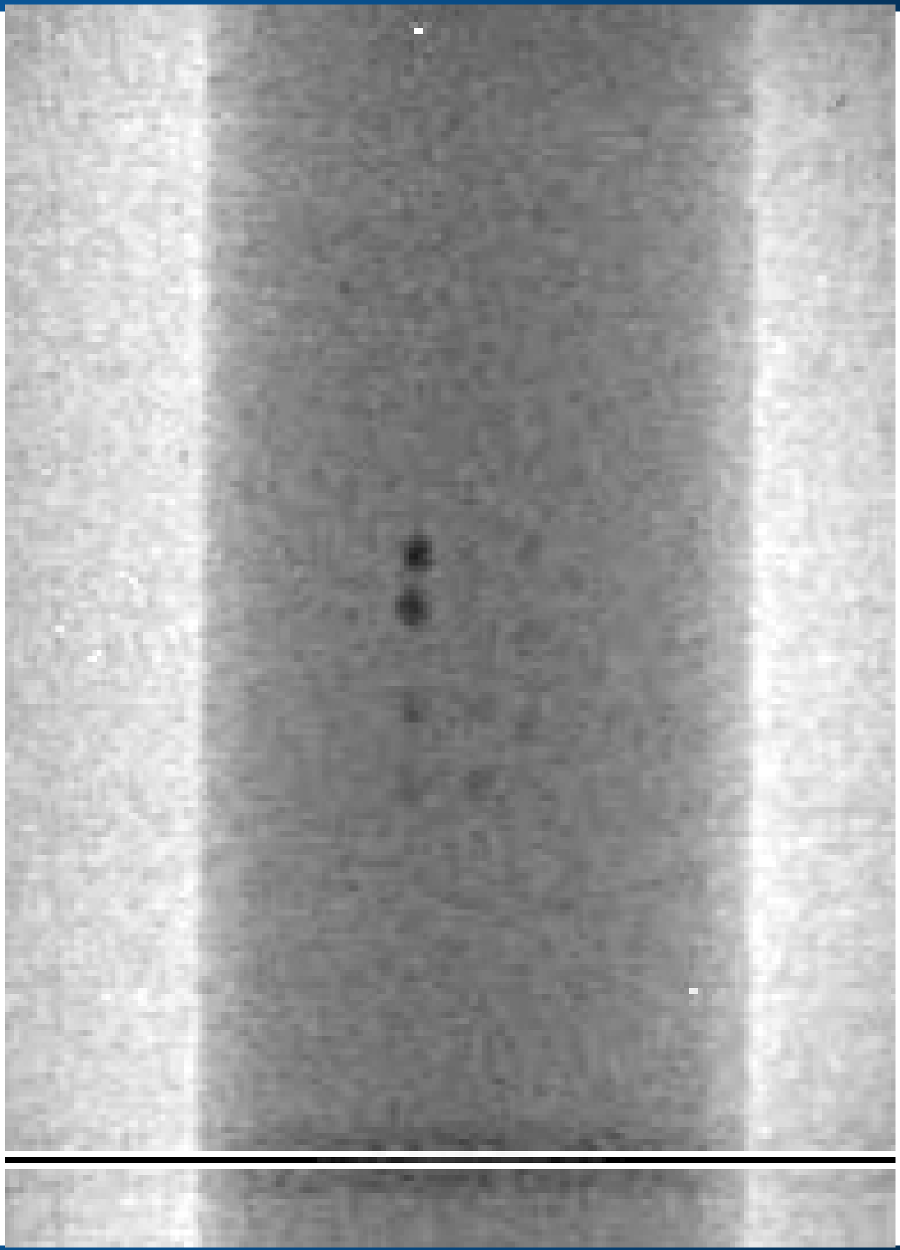


Fluorinert (FC-70)

Fluorinert (FC-70) was used as the calibrating fluid.

Static Fluorinert Radiography: Evaluating Sphere Materials





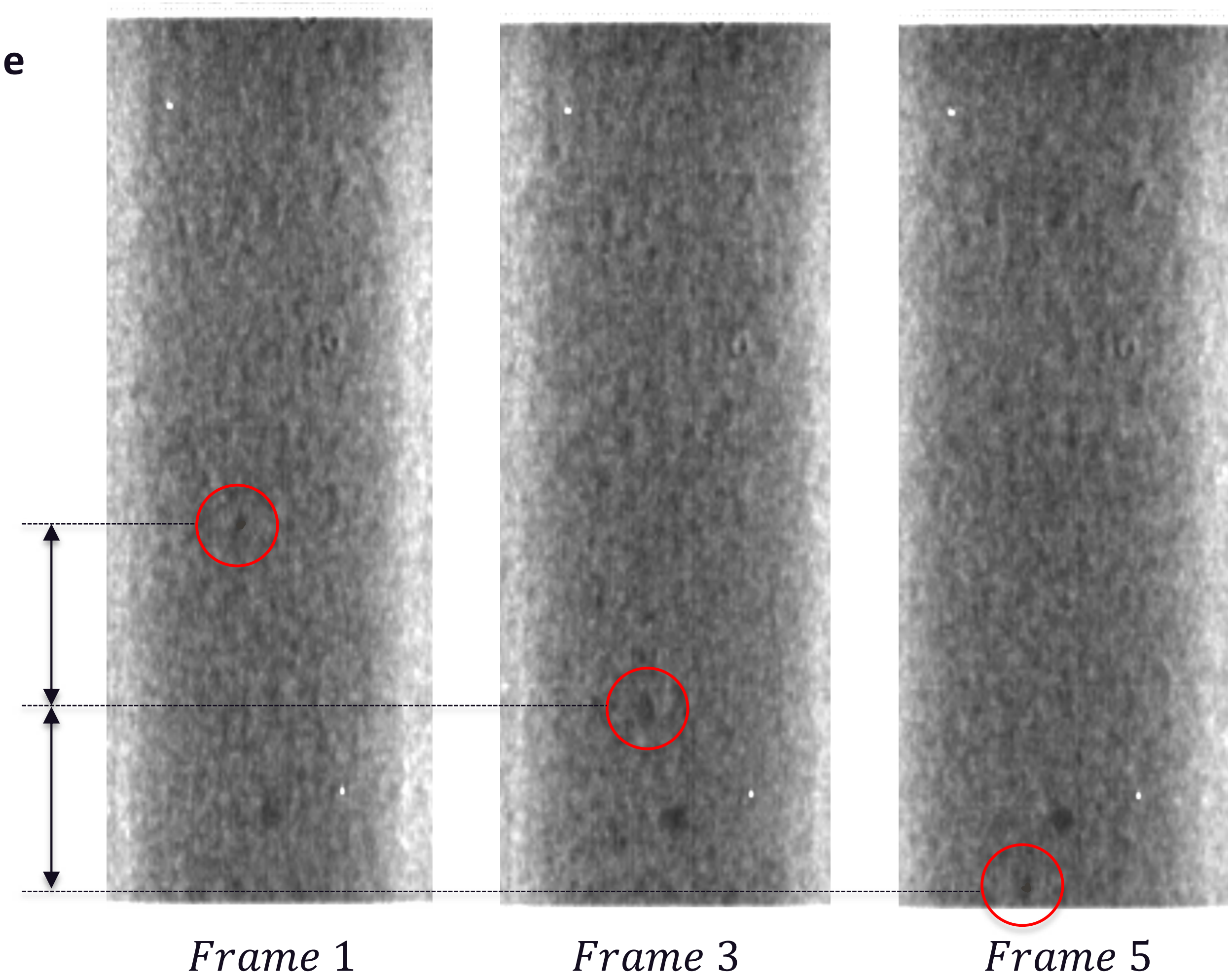
Fluorinert FC-70: Dynamic Viscosity (η) at Room Temperature

From the velocity of the sphere, the viscosity was calculated as follows:

$$\eta = \frac{2 \cdot g \cdot r_{sphere}^2 \left(\rho_{sphere} - \rho_{liquid}\right)}{9 \cdot v_{sphere}}$$

$$\rho_{liquid} = 1.9259\ g/cc$$
$$\rho_{borosilicate} = 2.23 g/cc$$
$$r_{sphere} = 1\ mm$$
$$g = 9.80665\ m/s^2$$

Temperature:	30 °C
Known viscosity:	**0.0173 *Pas***
Estimated Velocity:	38.98 *mm/sec* (25 °*C*)
Measured Velocity:	33.8 *mm/sec*
Measured Viscosity:	**0.0196 *Pas***



$Rate: 5\ frames\ per\ second$

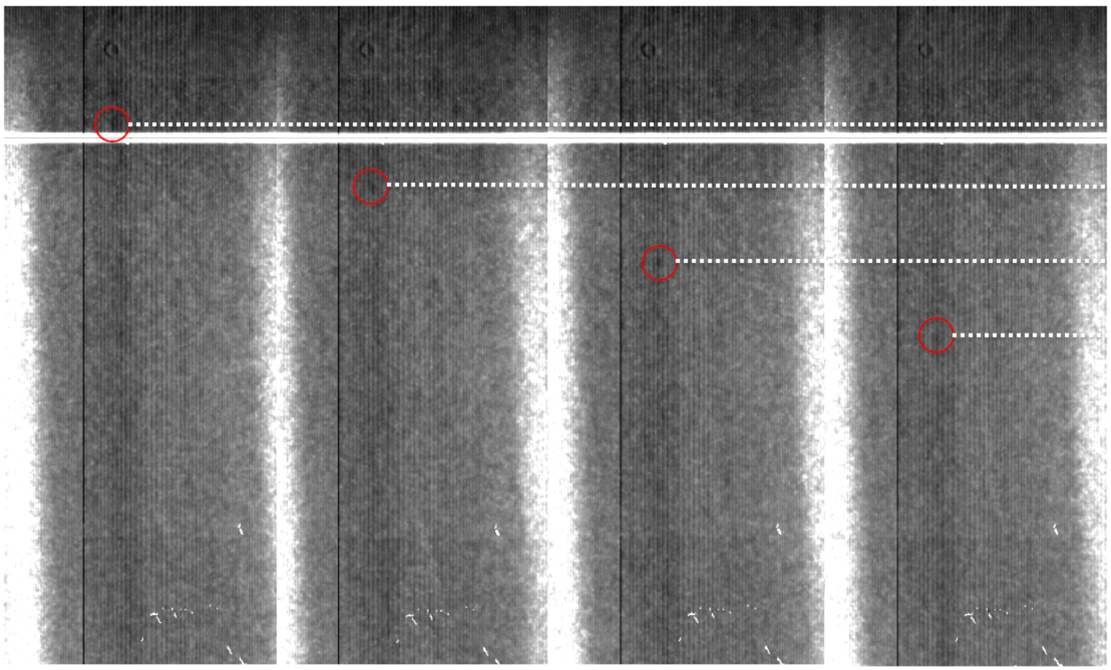
Viscosity: NaCl + 16.5wt%UCl_3

- Inert Atmosphere (flowing)
- Temp: 825 °C

$$\eta = \frac{2 \cdot g \cdot r_{sphere}^2 \left(\rho_{sphere} - \rho_{liquid}\right)}{9 \cdot v_{sphere}}$$

$$\rho_{liquid} = 2.0355\ g/cc$$
$$\rho_{borosilicate} = 2.23\ g/cc$$
$$r_{sphere} = 1\ mm$$
$$g = 9.80665\ m/s^2$$

- Measured Velocity: 1.38 cm/sec ±0.02 cm/sec
- Measured Viscosity: 0.030 Pas*
- **<u>There is no published data to compare to!</u>**
- Predictions/estimates were incorrect

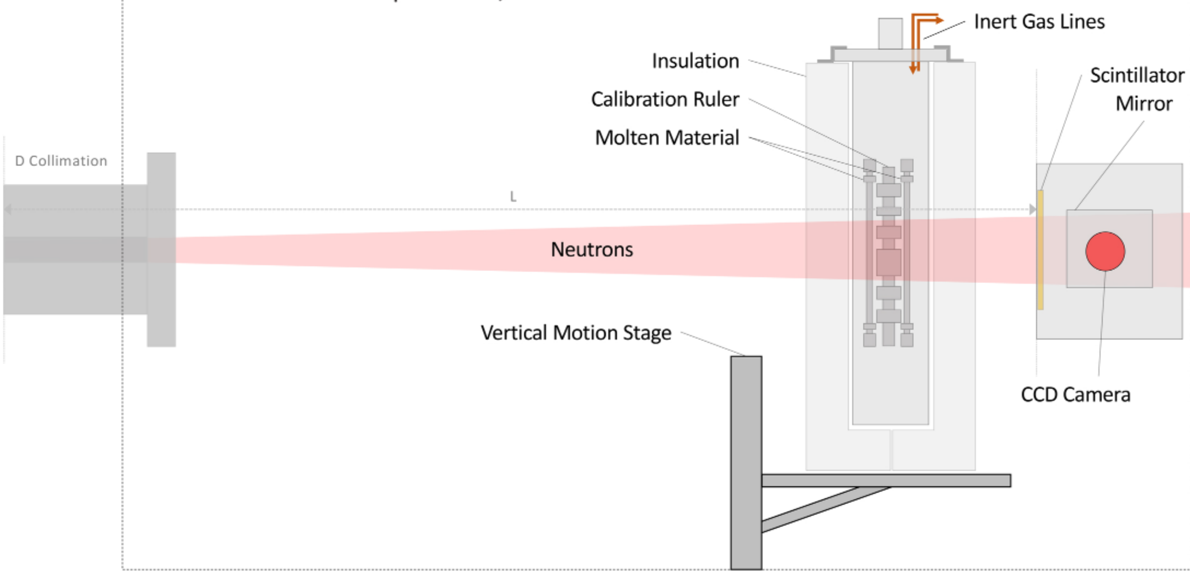


2 frames per sec

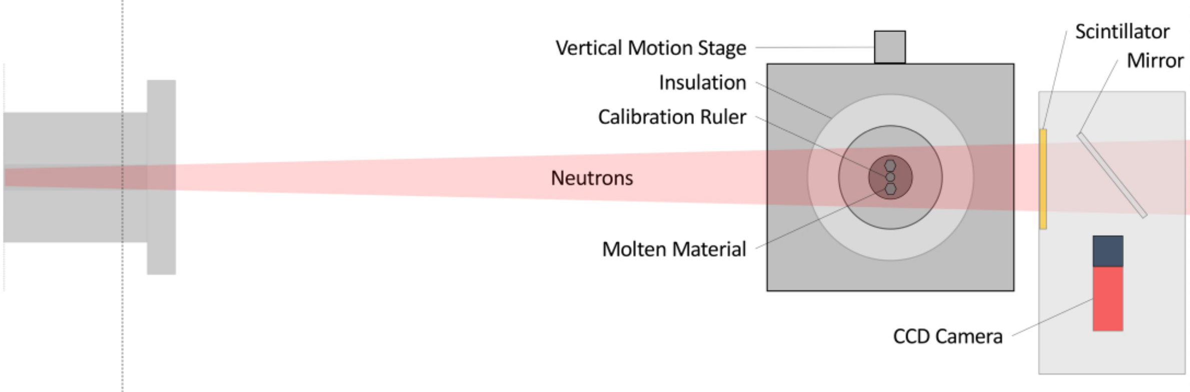
Average Measured Velocity: 1.38 cm/sec ±0.02 cm/sec

**required our density measurement*

Setup for Neutron Dilatometry Measurements



Side-On View of Setup in ERNI/FP05



Top-Down View of Setup in ERNI/FP05

Measurements were performed Fall 2019

Neutron Beam at FP5:

Neutron Energies:	Cold - Epithermal
Rep-rate:	20 Hz
Beam Area:	~9 cm^2 (on camera)

New High-Resolution Neutron Imaging Camera

Scintillation Plate:

Company/Model:	RC-TriTEC
Conversion Material:	Gd_2O_2S:Tb
Thickness:	20 μm
Resolution:	27 μm

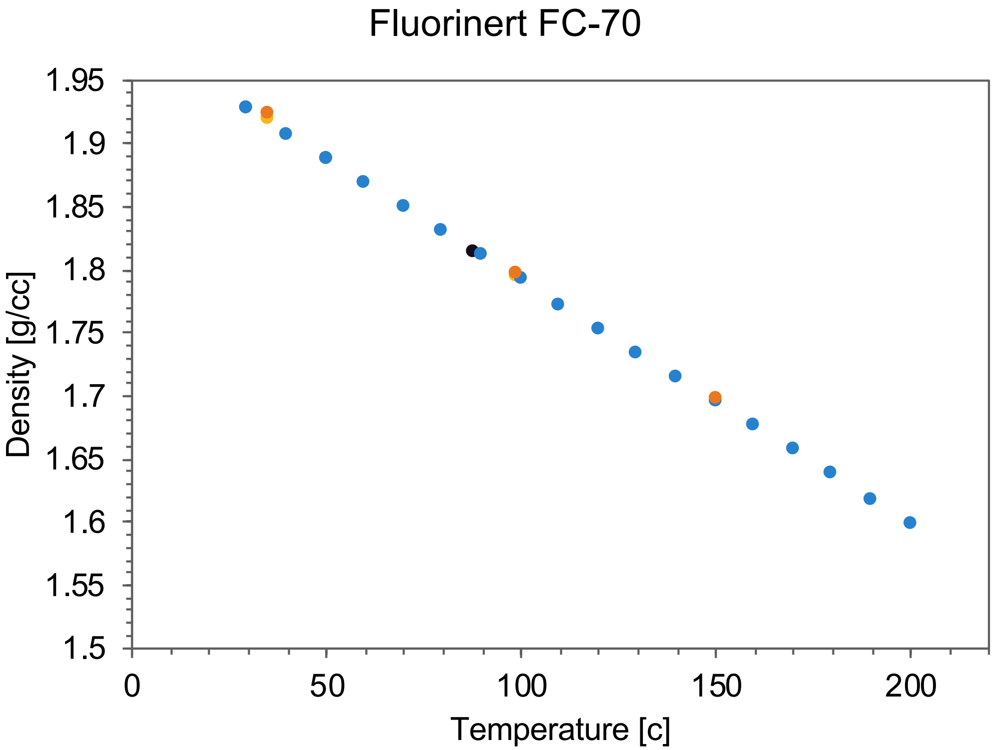
CCD Camera

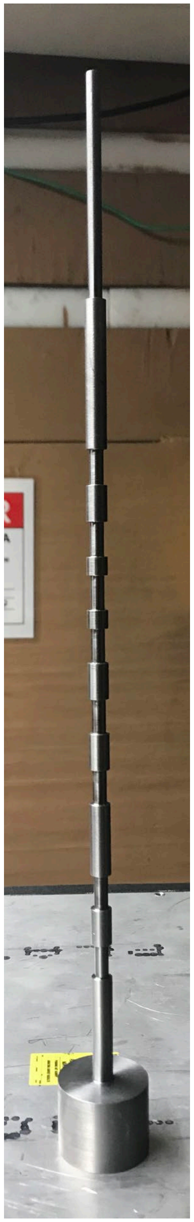
Company/Model:	ATIK 490ex
Pixel Matrix:	3379 x 2703
Pixel Pitch:	3.69 μm^2
Cooling:	Termoelectric
Average Exposure:	1 to 30 mins

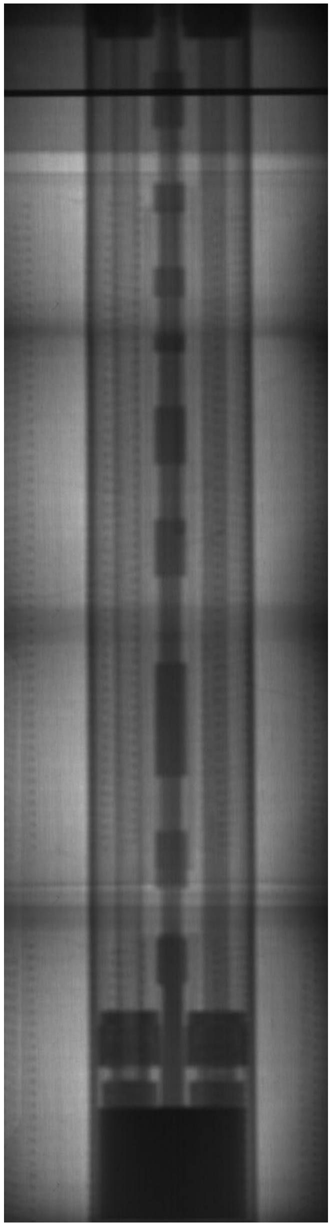
Density as a Function of Temperature: Fluorinert (FC-70)

- <u>Density a different way:</u> A well-characterized stainless steel capillary tube is used to contain the fluid; volume of a sample of known mass measured at different temperatures

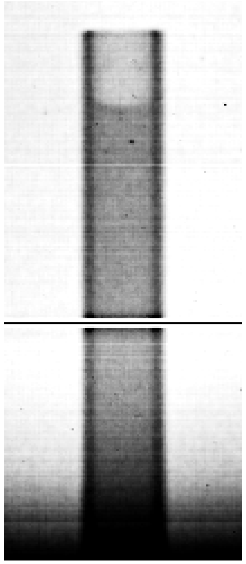
Compared with reference values, our measured density values are lower by only 0.05%
(Extrapolated error: < 0 .18%)







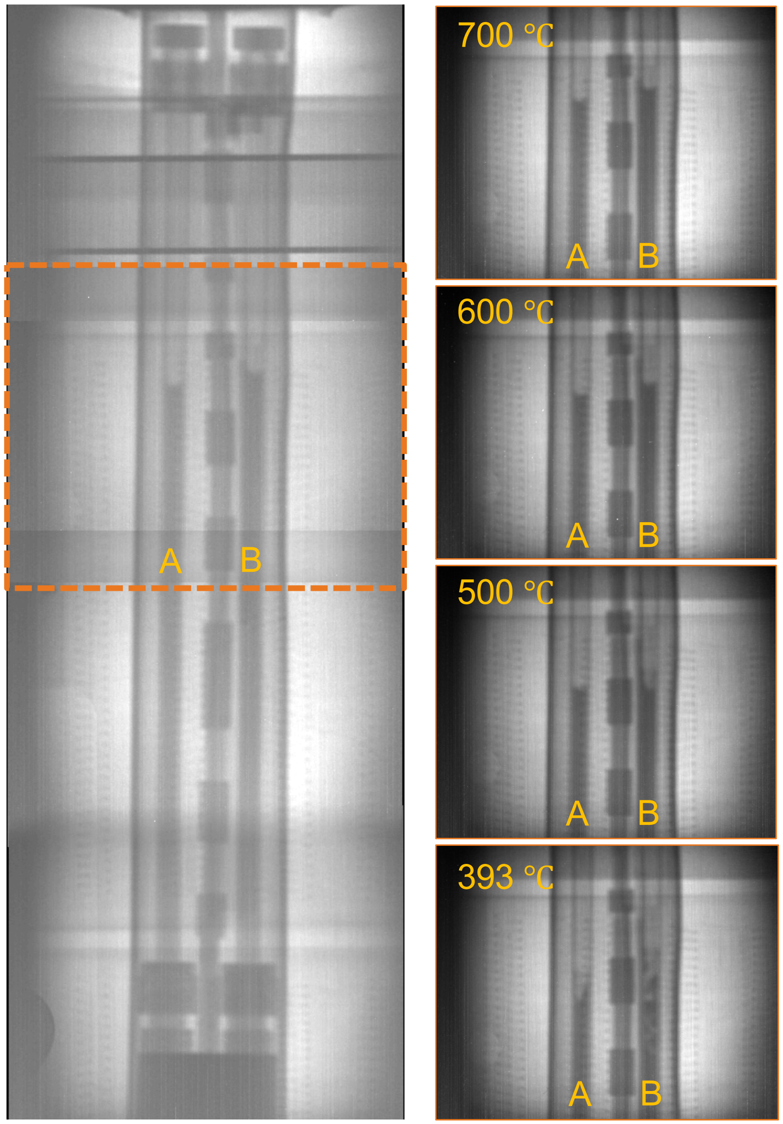
Meniscus



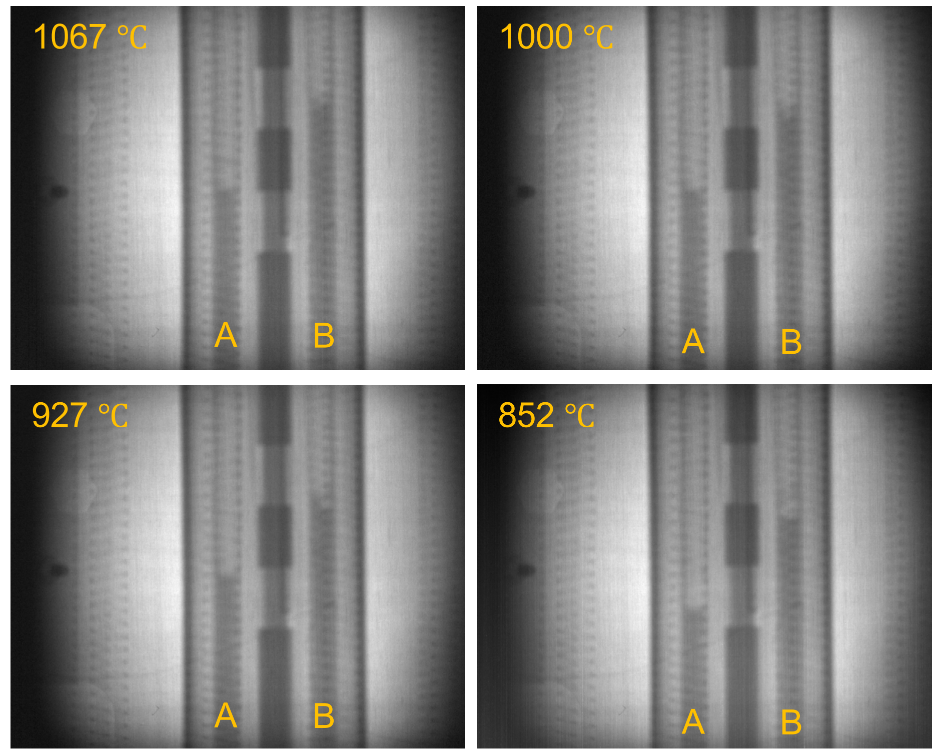
Scale and distances are measured with ImageJ

Neutron Dilatometry Measurements of Molten Salts

LiCl+KCl (A) and LiCl+KCl+ 5wt%UCl_3 (B)



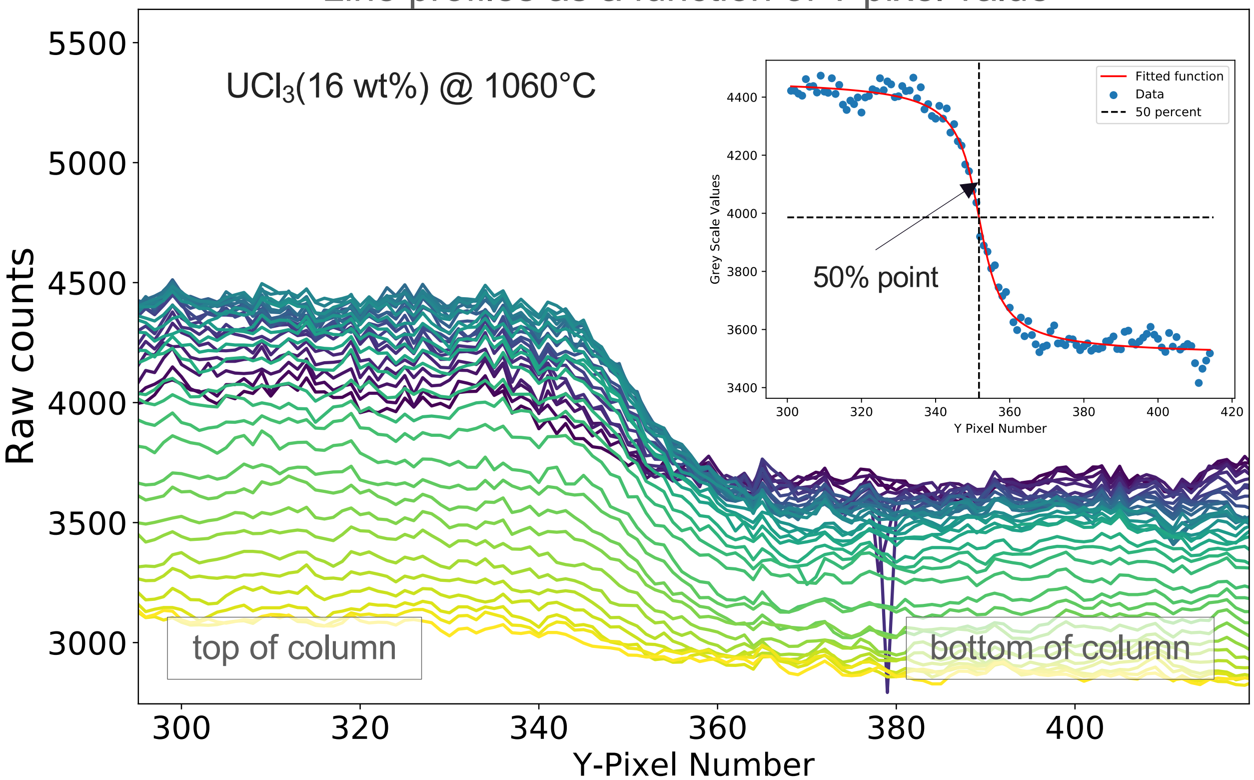
NaCl+ 90wt%UCl_3 (A) and NaCl+ 80wt%UCl_3 (B)

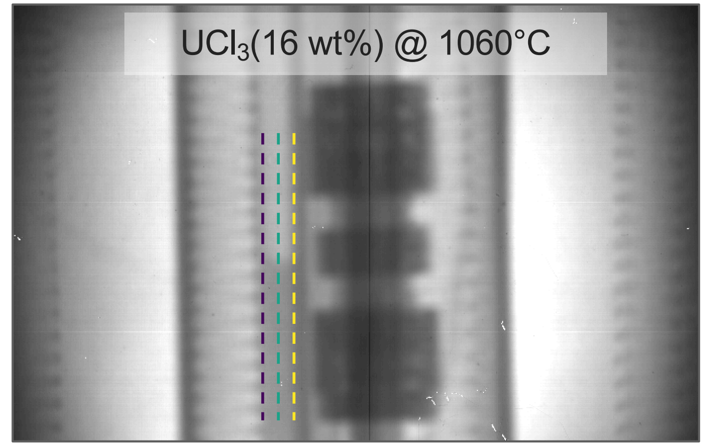


ImageJ Analysis of Neutron Dilatometry Measurements

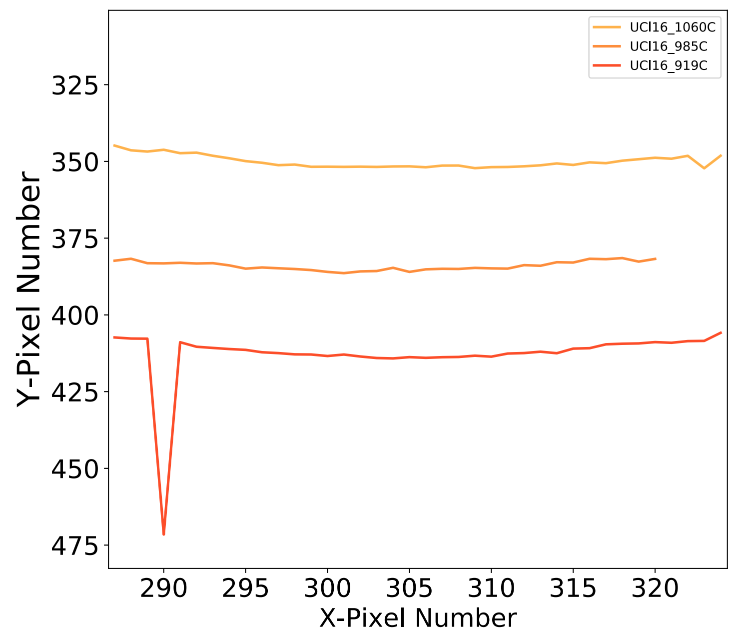
Mapping out the shape of the meniscus at each temperature
(allows for more accurate determination of molten material volumes)

Line profiles as a function of Y-pixel value



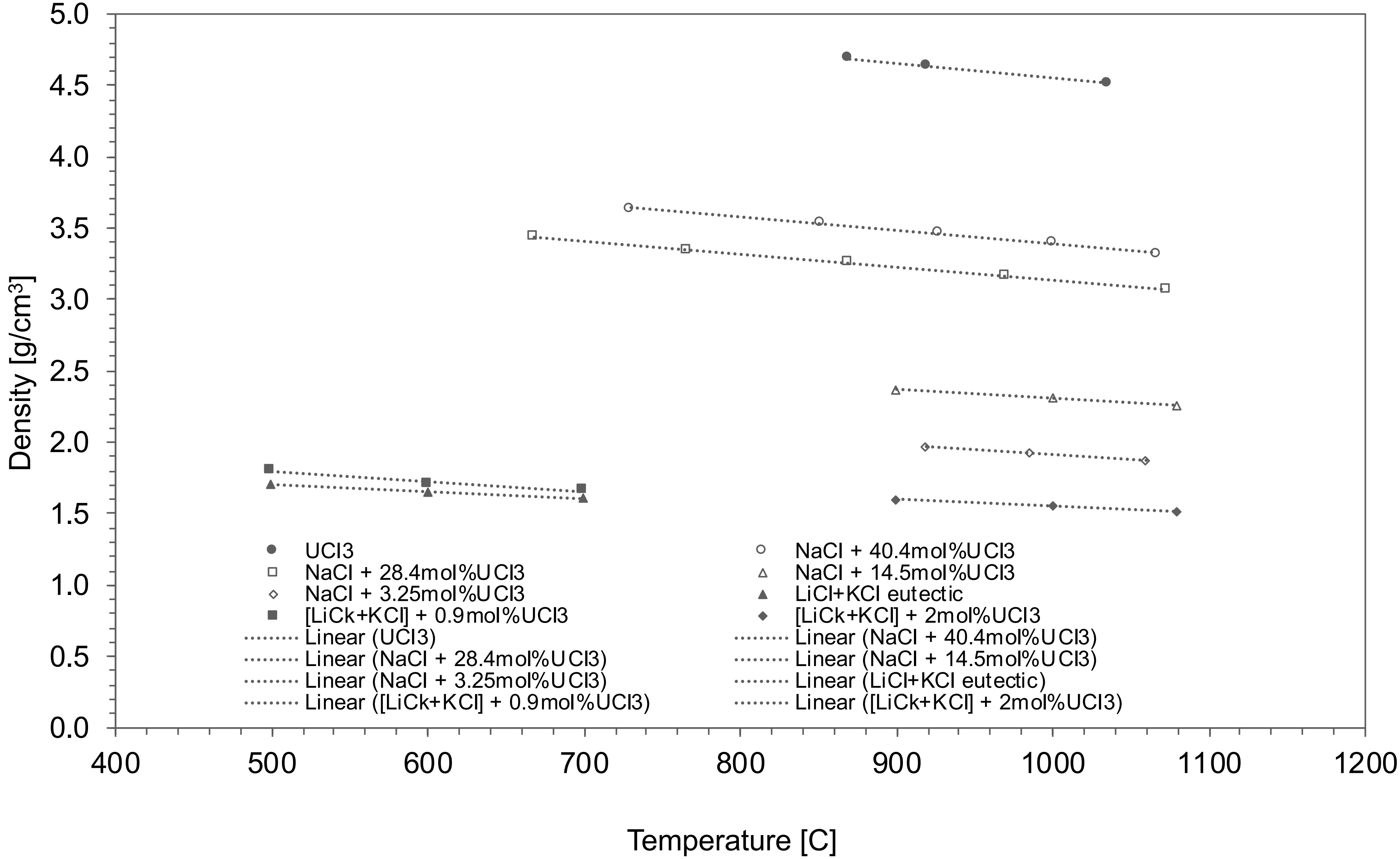


Meniscus growth as a function of temperature in UCl_3(16 wt%) +NaCl



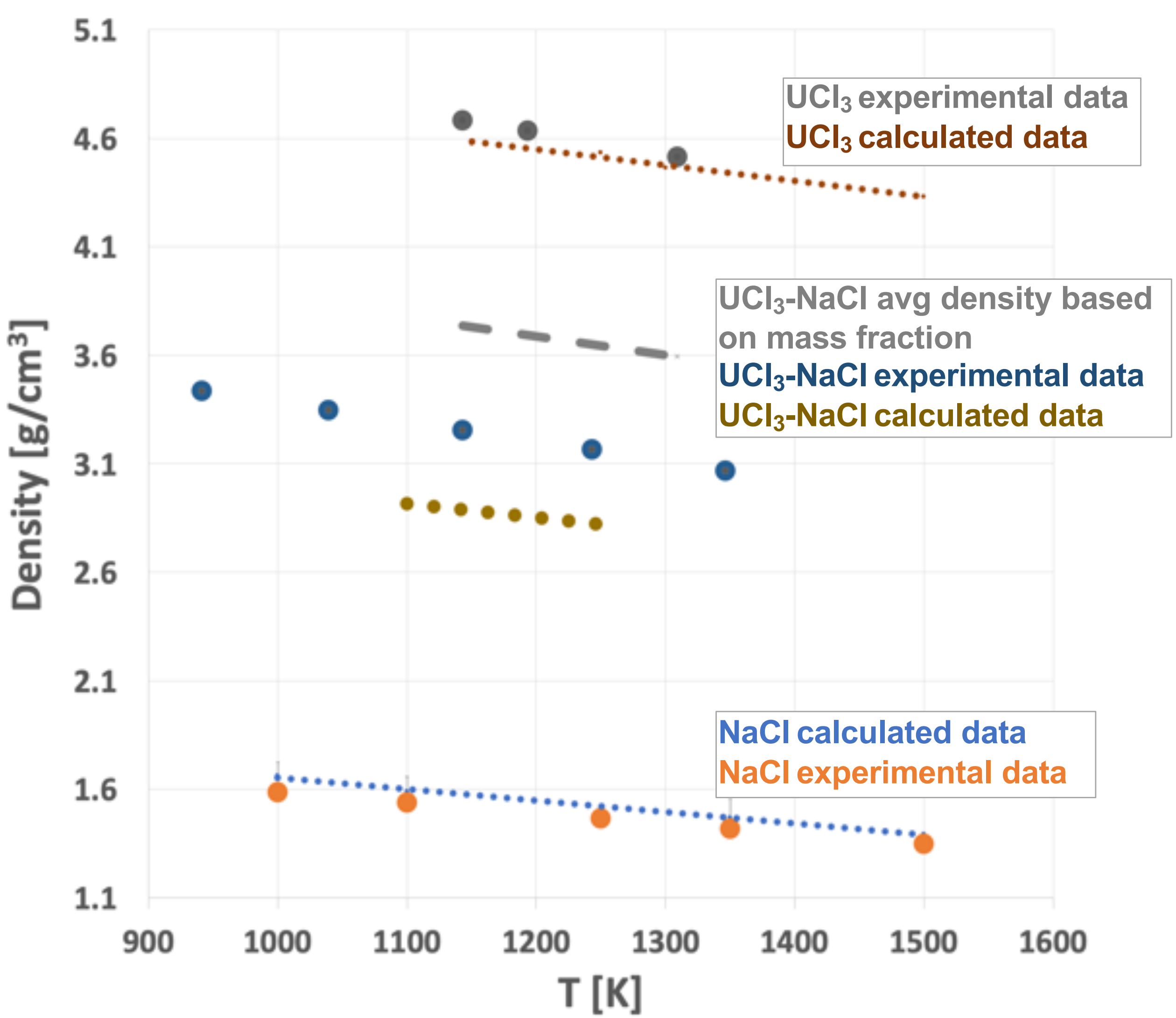
This technique can be expanded to include uncertainty analysis!

Summary of Molten Chloride Neutron Dilatometry Experiments



Integrating Modeling with Empirical Density Results

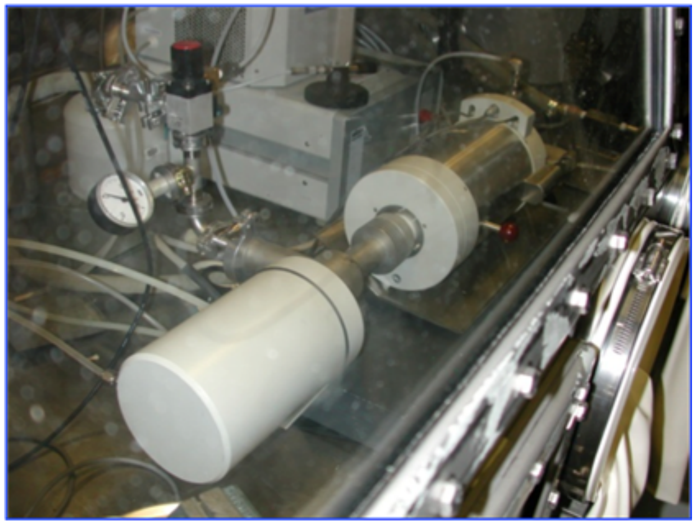
- Top and bottom sets of data: pure UCl_3 and NaCl
  - Modeling data close to experimental data
- Center set of data: 28 mol% UCl_3 in NaCl
  - Experimental data (blue dots) *lower* than simple average density based on mass fraction (gray trace)
  - Modeling data not as close for mixture as for pure systems; required incorporation of Van der Waals interactions and magnetism
  - These observations are prompting the next stages of our research!



Conventional Dilatometry

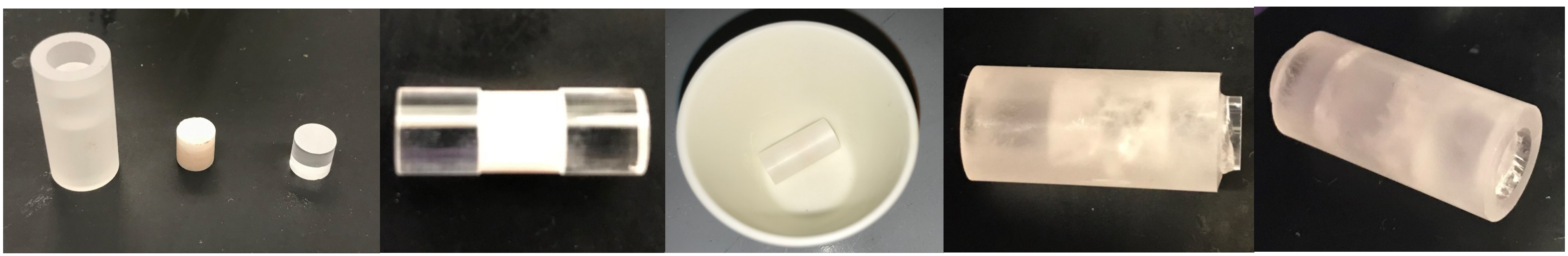
Netzsch 402C
LVDT

-160-500 °C
RT-1600 °C
Single sample



Push-rod dilatometer;
Used on Pu metal samples

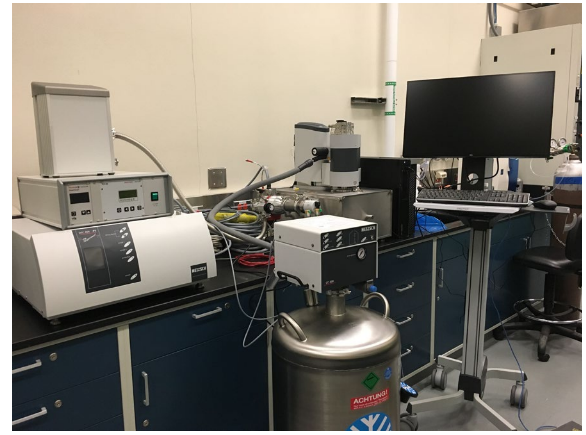
- Complements neutron dilatometry – higher throughput
- Plutonium instrument available
- Preliminary testing underway



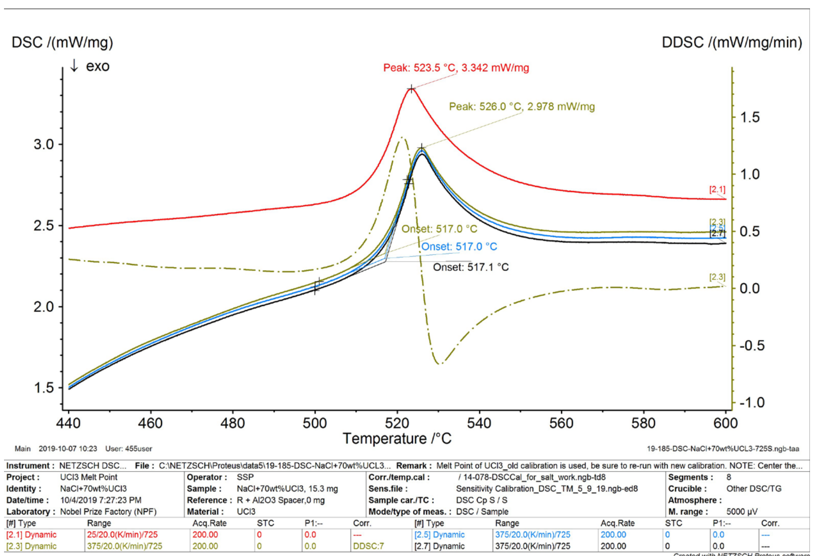
First sample holder tests: varied salt type, pellet size, temperature, materials of construction

Differential Scanning Calorimetry (DSC)

- Determine liquidus/solidus transition temperatures (**melt point**, T_m)
- Assess thermal stability based on endothermic/exothermic events
- Plutonium instrument available
- **Our current status:**
  - Calibrated for high temperature (400-1100 ^{o}C) measurements on molten chloride salts
  - Uranium-molten salt melt points collected; next step is to take heat capacity measurements (standards made)

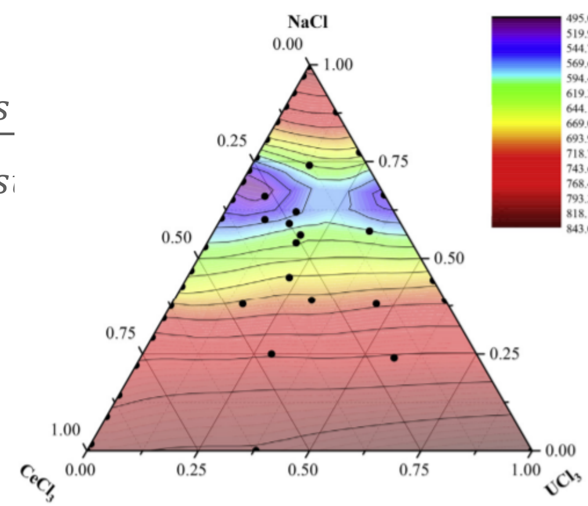


Netzsch DSC 404 F1 Pegasus
Max temp: 1650 °C



NaCl + 70 wt% UCl_3 (T_m = 517 °C)

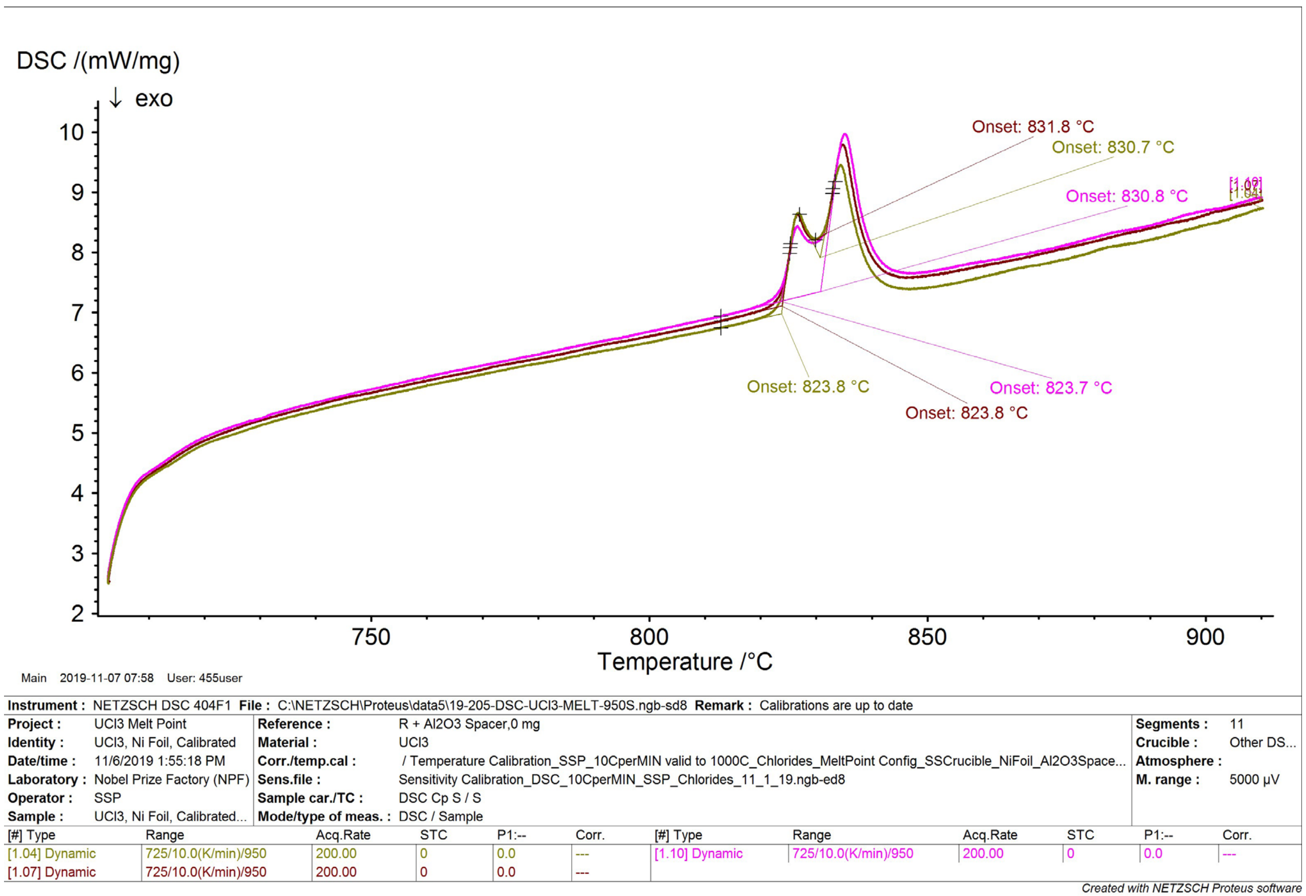
$$C_{ps} = C_{pst}\frac{\Delta q_s}{\Delta q_{st}}$$



Contour map of the experimental data measured for the NaCl-UCl_3-$CeCl_3$ system.

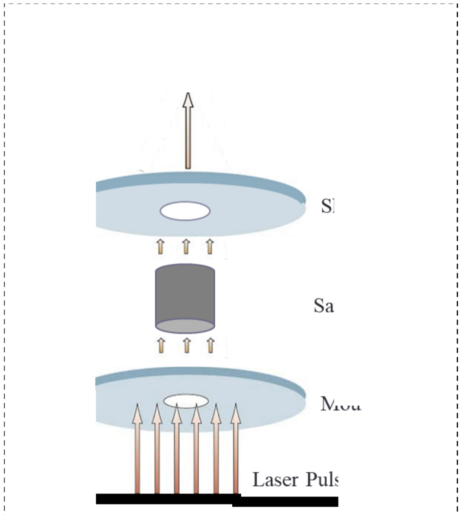
Sooby, E. S.; Nelson, A. T.; White, J. T.; McIntyre, P. M., Measurements of the liquidus surface and solidus transitions of the NaCl–UCl_3 and NaCl–UCl_3–$CeCl_3$ phase diagrams. *J. Nucl. Mater.* **2015,** *466*, 280-285.

Using Melt Point to Determine Sample Purity

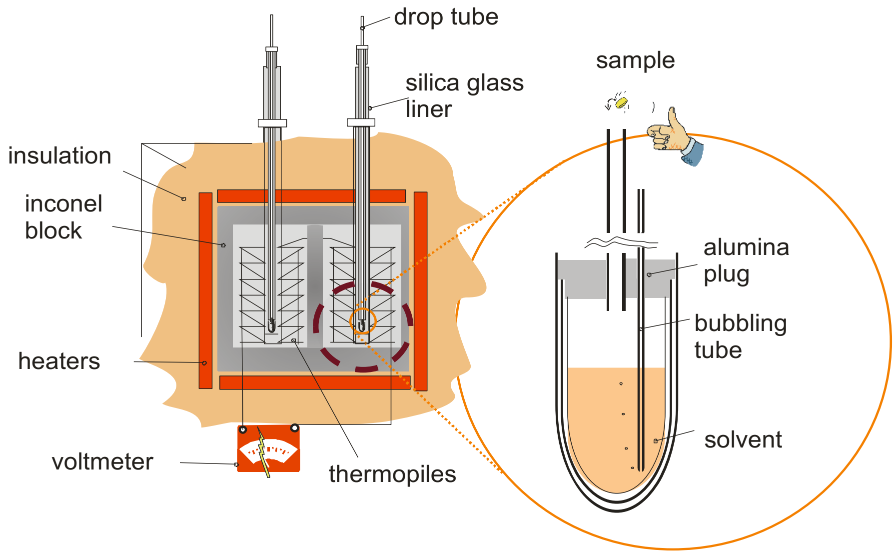


- With this new capability for measuring actinide molten salts, can determine **sample purity** of molten actinide salts (here, an old sample of UCl_3 from Y-12 is found to be impure)
- Will be useful for post-radiography experiments

Planning & Preparation Stage: Laser Flash Analysis (LFA) and Drop Calorimetry



$$\frac{\partial T}{\partial t} = \alpha_D \nabla^2 T \quad \left[{m^2}/{sec}\right]$$

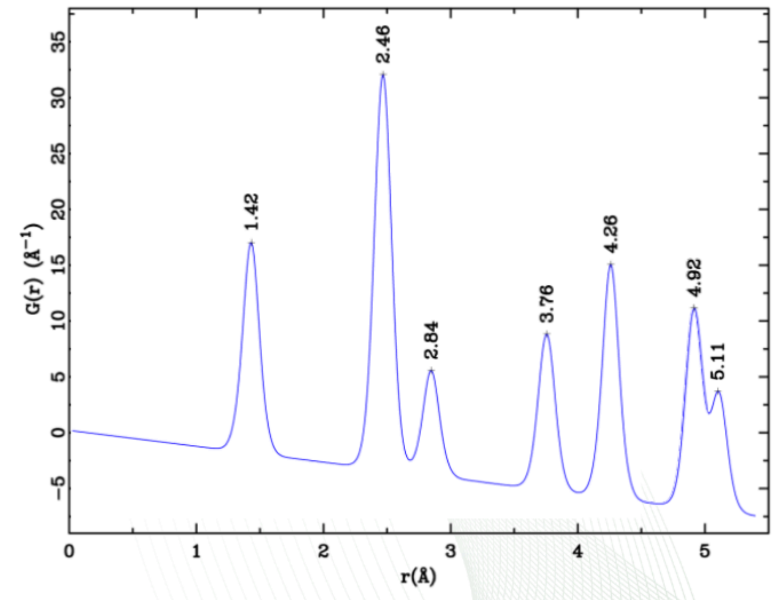


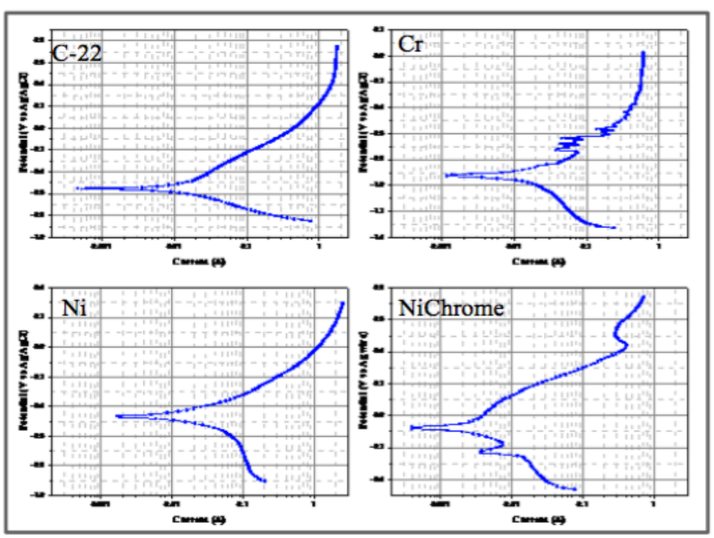
- The **laser flash analysis (LFA)** technique is currently the most widely accepted method for precise measurement of thermal diffusivity
- LFA has been adapted for the study of liquid metals, but to date there is no published LFA data on actinide-molten salts
- Current work: sample holder design
  - Must address radial heat loss due to convection
  - Plan is to increase one-dimensional heat flow, while remaining sealed against pressurization and high temperature

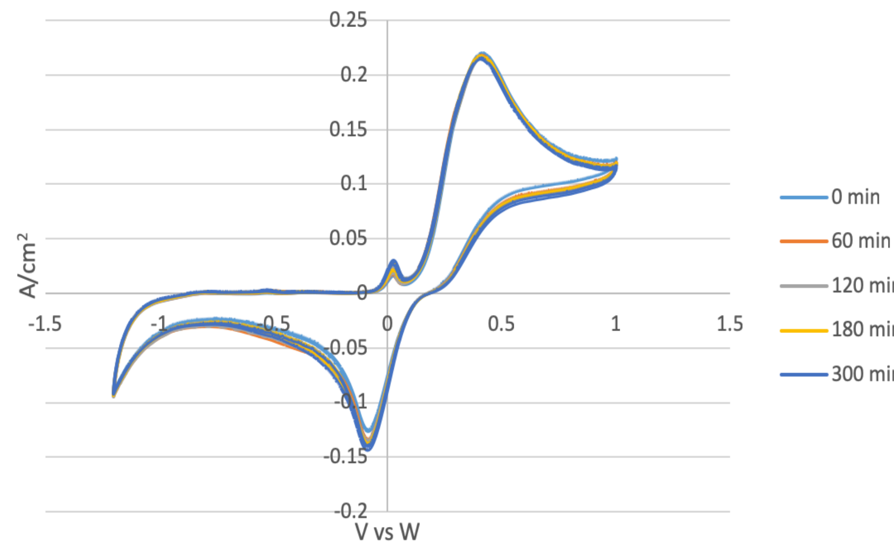
- Schematic of high-temperature twin Calvet-type calorimeter—unique to LANL (EES Division, Hongwu Xu)
  - *Enlarged region:* assembly for **drop solution calorimetry** in molten solvent
- Provides heat of dissolution, and enthalpies of mixing
- Demonstrated on plutonium samples; goal is to adapt for molten salt

Chemical Properties

- **Local Structure Experiments (Planned)**
  - Neutron Pair Distribution Function Analysis
  - Raman Spectroscopy
- **Speciation and Impurity Chemistry (Ongoing)**
  - Cyclic Voltammetry
  - Square Wave Voltammetry
- **Corrosion and Materials Evaluation**
  - Cyclic Potentiodynamic Polarization
  - Static and pseudo-dynamic exposure







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Resources & Contact Info

1663 Article on Monreal-Jackson Molten Salt Research, “Refueling the Reactor”, January 2020
https://www.lanl.gov/discover/publications/1663/2020-january/refueling-the-reactor.php

The Nuclear Powered Plane – YouTube Video
https://www.youtube.com/watch?v=9Jt924xjaJo

DOE-NE Advanced Nuclear Reactor Articles (with mentions of MSRs):
https://www.energy.gov/ne/articles/swipe-right-nuclear-6-eligible-advanced-technologies
https://www.energy.gov/ne/articles/3-advanced-reactor-systems-watch-2030
https://factsheets.inl.gov/FactSheets/molten-salt-reactor.pdf

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